

Spontaneous symmetry breaking by double lithium adsorption in polyacenes

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Abstract

We show that adsorption of one lithium atom to polyacenes, i.e. chains of linearly fused benzene rings, will cause such chains to be slightly deformed. If we adsorb a second identical atom on the opposite side of the same ring, this deformation is dramatically enhanced despite the fact that a symmetric configuration seems possible. We argue, that this may be due to an instability of the Jahn-Teller type possibly indeed to a Peierls instability.

Keywords: Graphene, DFT, Hartree Fock

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1 INTRODUCTION

Sheets, strings and tubes of hexagonal carbon structures have received an increasing amount of attention ever since the discovery of Fullerenes [1]. In particular the question of adsorption of electron donors has been discussed in various contexts [2, 3]. The starting points of our consideration was a molecular study of small carbon sheets, treated as aromatic molecules with hydrogen termination at the edges [4] as well as a study on larger flakes [5]. We shall focus on one effect mentioned in [4], namely the deformation of such structures under adsorption of one and two lithium atoms. In [5] it was pointed out, that such deformations are far more pronounced if we have approximately symmetric adsorption on both sides of the sheet. By considering a chain, i.e. a polyacene, we simplify the problem and this will allow us to get a clearer view and better understanding of the reasons for the symmetry breaking.

We perform numerical calculations using one standard code both on the Hartree Fock (HF) level and on the density functional theory (DFT) level. As in [4] we find qualitative agreement between both calculations, which indicates that the deformations observed in our calculations, are not too sensitive to the accuracy of the method used, yet differences in the deformation angle will be seen. Indeed the symmetry breaking deformation occurs even more clearly in polyacenes, and evidence points to a Jahn-Teller [6] like effect. We briefly revisit the proof of Ruch and Schoenhofer [7] to see, that this is plausible. As the system is quasi one-dimensional this effect might be reduced to a somewhat unusual Peierls distortion[8].

The paper will be organized as follows: In the next section we shall discuss the configurations we shall use and the numerical tools that will be applied to obtain the results which we present in the third section. In the forth section we comment our findings from a group theoretical point of view and finally we shall give an outlook on the implications for other systems and on planned additional work.

2 CONFIGURATIONS AND COMPUTATIONAL TOOLS

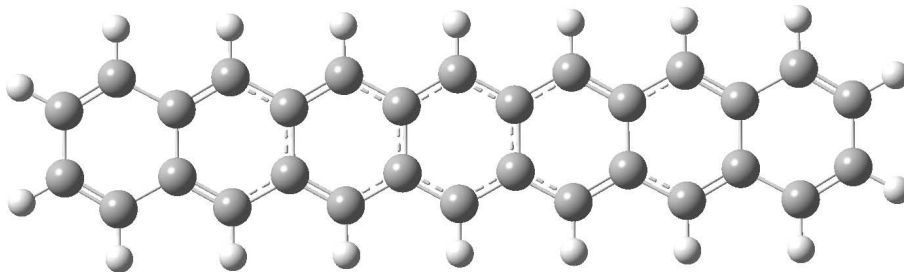


Figure 1: The heptacene molecule

As a simpler way to attack the problems of symmetry breaking discussed in [4, 5] we shall focus on polyacenes or acenes, i.e. chains of simple benzene like hexagonal carbon structures bounded by hydrogen atoms. Though we calculated chains with length from three (anthracene) to nine rings (nonacene), we shall concentrate on showing heptacene, i.e. chains of seven rings as illustrated in Figure 2. Other polyacenes show analogous results using the methods described below. The structure is flat (not shown) and deformations of the rings at the ends of the chain are small and imperceptible on the figure. For pentacene an atomic-force microscopy picture is available [9].

The purpose of the calculation will be to analyze the stability of such configurations when lithium atoms are adsorbed. Note that practically speaking structures beyond pentacene are very reactive, but this does not concern us here. We shall keep in mind, that in [4, 5] such deformations were greatly enhanced by adsorbing a lithium atom on opposite sides of the same carbon ring. Calculations for the larger configurations are quite demanding, and we have used the super-computing facilities of DGSCA of the University of Mexico (UNAM).

The calculations were performed with the GAUSSIAN09 program codes [10]. Geometry optimizations were performed with the Hartree-Fock (HF) method [11, 12] as well as with DFT [13] and the agreements and differences of the two methods will be discussed.

We have chosen the 3-21G* basis in which the 1s AO (Atomic Orbitals) of a first-row element is represented by a fixed combination of 3 GTO's (orbitals are approximated by a linear combina-

tion of gaussian basis functions), the 2s (2px etc.) are approximated by a fixed combination of 2 GTO's and the extra valence orbitals 2s'(2px' etc.) are just one GTO. The 3-21G basis set offers a reasonable compromise between computational burden and quality of results. Calculations carried beyond the Hartree Fock level by density functional theory (DFT) computations. The B3LYP method [14] was used both with the above basis sets and with the basis sets 6-31G* (6-31G + d-functions for first row atoms). This method uses the Becke three parameter hybrid functionals which are composed of $A * E_{X\text{Slater}} + (1 - A) * E_{X\text{HF}} + B * \Delta E_{X\text{Becke}} + E_{C\text{VWN}} + C * \Delta E_{C\text{non-local}}$ by which A, B and C are the constants determined by Becke and suitable for the G1 molecular set.

3 SINGLE AND DOUBLE ADSORPTION

We shall now proceed to study the effects of single and double adsorption of lithium at a single carbon ring of heptacene. Double adsorption to the same ring is known to be possible only if the two adsorbed atoms are at opposite sides. We shall mainly show density functional calculation with the 6-31G* basis set and we shall see that the results are qualitatively equal to those of Hartree Fock calculations. Note that they are also qualitatively equal and quantitatively very to DFT calculations with the 3-21G* basis sets.

As expected for single Li adsorption the deformations of the molecule are slight, as seen in Fig. 2 for different choice of the ring to which we adsorb.

We thus proceed to use these structures as starting points for the calculation of the adsorption of the second Lithium atom to the other side of same the ring to which the first Lithium was adsorbed.

The result shown in Fig. 3 is spectacular. The deformation has increased greatly, and as compared to [4, 5] it is much better defined, because the effect on a chain, i.e. on a polyacene is not local but global. If this were sheet, strong bonds of far lying rings would maintain global properties. Thus only a local distortion could occur. As a symmetric structure seems possible, what we see is clearly spontaneous symmetry breaking of one kind or another. By first depositing one Lithium atom which produces a slight deformation we determine to which side the chain will bend. This was tested explicitly, but we will not show the corresponding calculation, as the result is rather obvious. Yet, as a caveat, we mention that, if we add both lithium atoms simultaneously, the "Gaussian" code does not always find the asymmetric configuration despite of its energy advantage. Instead it can remain in a symmetric configuration. This seems to point to a small local minimum of energy. This will be explored in a future publication.

In order to demonstrate the robustness of the result we shall show in Fig. 4 that the double adsorption case behaves qualitatively similar whether we use DFT or HF. In Fig 4a we see the DFT result shown already in the previous figure, while in part *b* we see the equivalent HF calculation. Clearly the angle between the flat configuration and the calculated one is bigger in the Hartree Fock case; this fact seems to indicate that the symmetry breaking is a mean field effect, which is actually somewhat mitigated by correlations.

In table 1 we show the the angle of deviation form the flat configuration for adsorption on rings 1,2,3 and 4 (center) both for the DFT and the HF calculations. This angle is illustrated for the case of position 4 in Fig 4. We notice, that the larger angles for HF as compared to DFT are a

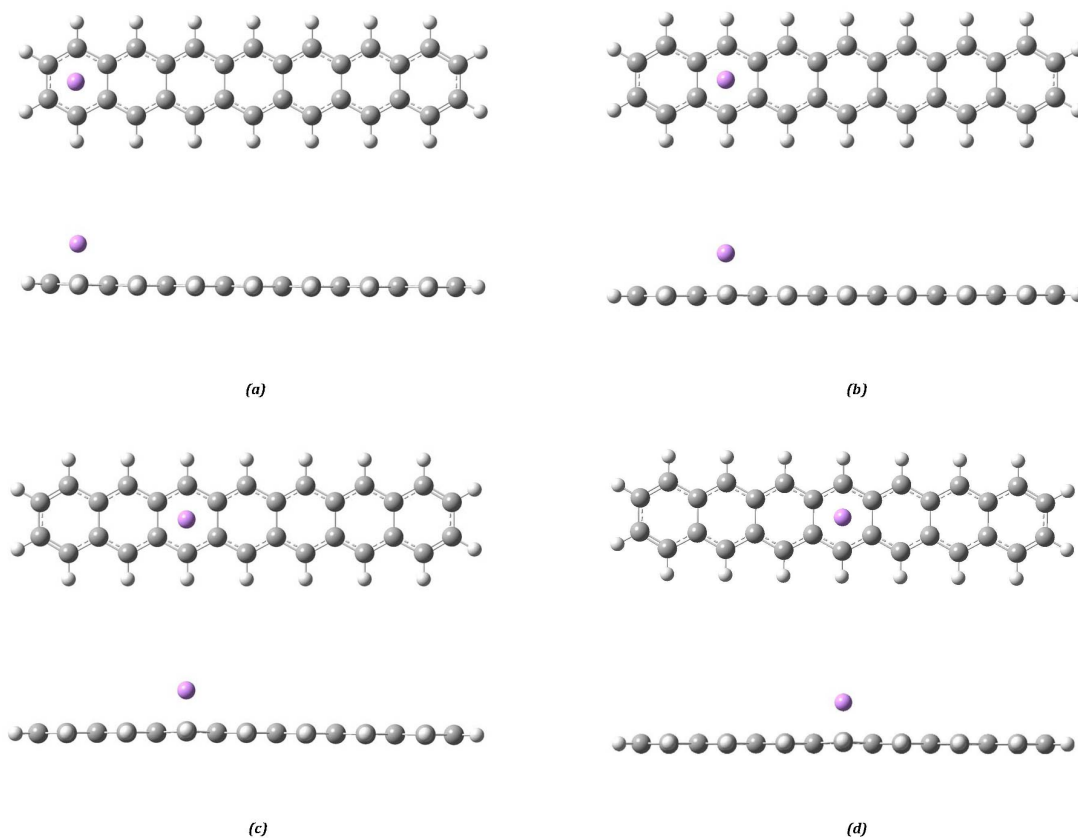


Figure 2: Chain of seven rings with one Lithium atom (a) adsorbed to the first ring, (b) the second ring, (c) the third ring and (d) the fourth ring,

systematic feature. For HF the angle diminished as we use a less symmetric configuration, while it changes little for DFT. We made the same DFT calculations using the basis sets 3-21G* and we did not find big differences in the angles.

If we have an even number of rings, there is no "center ring" and thus the most symmetric configuration does not exist. To demonstrate that this is not relevant we show in Fig. 3 one DFT (6-31G* basis sets) calculation for hexacene and see that there is no qualitative difference. Finally we note that adsorption of two lithium atoms to different rings, whether they are on one side or on opposite sides, does not display very different effects as compared to the adsorption of a single atom, except that the effect occurs on each of the sites. A detailed analysis of the stability of double adsorption to neighboring sites is still missing.

In view of the fact that this volume concentrates on symmetry we shall abstain from discussing more chemical aspects such as separation energies or the exact geometry of the adsorption well. As for the interesting question of mobility of the adsorbed atoms [15] we only wish to point to the global deformation, which would make a large scale movement necessary, if we move one

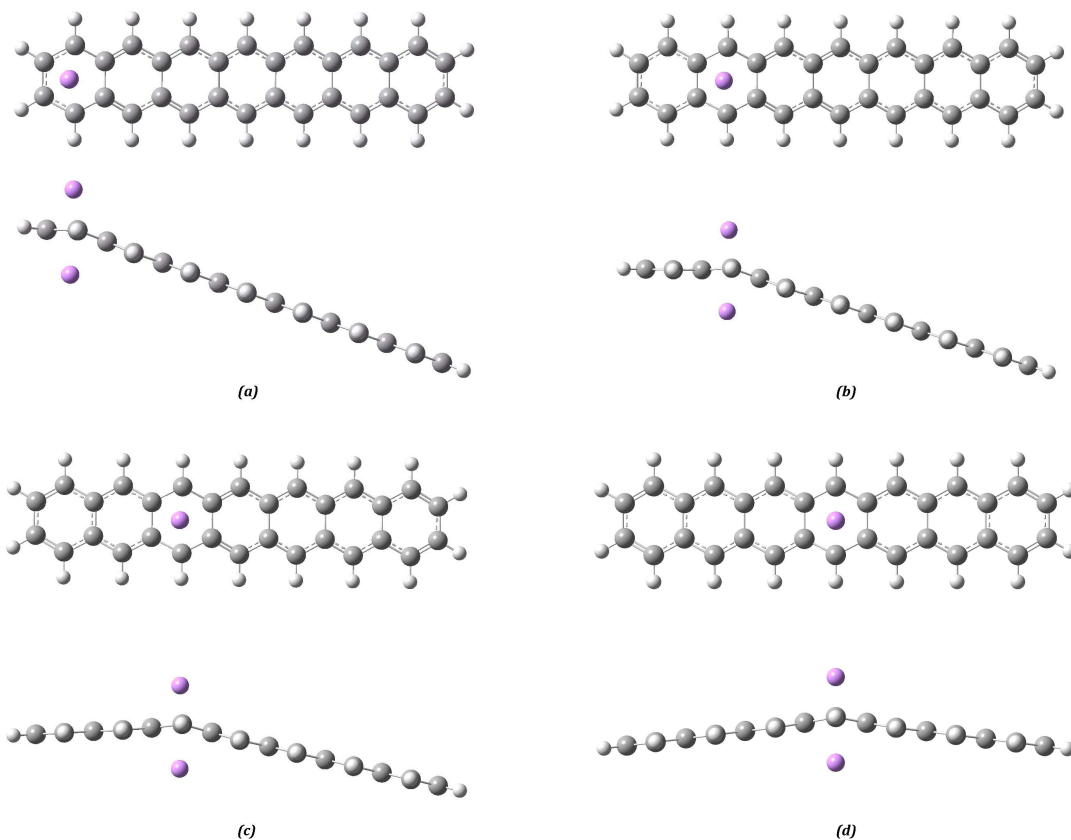


Figure 3: Chain of seven rings with two Lithium atoms (a) adsorbed to the first ring, (b) the second ring, (c) the third ring and (d) the fourth ring,

lithium atom. Thus it might well be, that the movement of a correlated pair of two lithium atoms is more mobile than a single one. At this point, this is speculation, though it may be worthwhile investigating the question in the future. We therefore in the next section will try to interpret our qualitative findings by group theoretical means.

4 A GENERALIZED JAHN-TELLER EFFECT OR PEIERLS DISTORTION?

We briefly recall, that Jahn and Teller predict instability of the symmetric configuration for certain molecules or complexes with respect to some point groups which might have been expected to be a symmetry groups. As we are dealing with a quasi 1-D system, it is worthwhile to mention, that the Peierls distortion is often viewed as the equivalent to the Jahn-Teller effect in one dimension. Yet as far a brief review of the literature tells us, Peierls distortion has been considered for one-dimensional distortions of the one-dimensional order, such as dimerization. Here we find for the quasi 1-D situation a deformation which bends the system, i.e. which

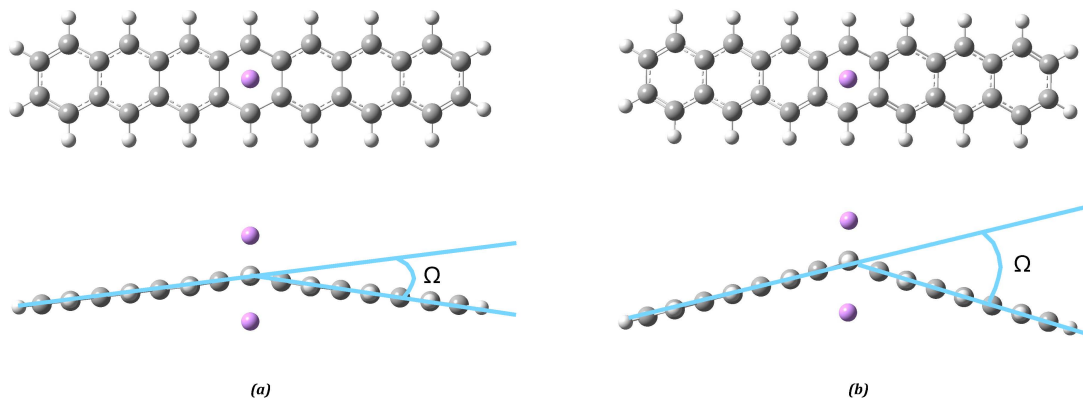


Figure 4: Heptacene with two lithium atoms adsorbed on opposite sides of the central ring. (a) shows the DFT calculation and illustrates the bending angle shown in table 1. (b) shows the HF calculation and also illustrates the bending angle shown in table 1.

Angle of deformation Ω		
POSITION	HF	DFT
1	19.17	19.77
2	27.75	21.18
3	33.99	20.33
4	36.29	18.86

Table 1: Angles deformation from flat heptacene vs position of the pair of lithium adsorbed to the the chain for positions 1, 2, 3 and 4 (center).

deforms it perpendicular to its extension.

We shall thus attempt to understand this deformation in terms of a generic derivation of the Jahn-Teller effect which was also invoked for the 2-D system [5]. Ruch and Schoenhofer [7] showed in a very general framework that whenever a molecular system, susceptible to be treated in Born-Oppenheimer approximation, had a symmetry group made up of a semi-direct product of two groups, we would find that the nuclear skeleton would be unstable and destroy the symmetry in one factor if the electron density would violate the symmetry of the other factor. The generalization of this argument is a challenge that has come up in this context, and we shall take up this matter in a future paper. Here we shall limit ourselves to a plausibility argument based on the work of Ruch and Schoenhofer, which indicates how a complicated, and in Moshinsky's terminology "messy" problem might be solved with deep and elegant group theoretical techniques.

In the present case we assume that our chains mimic symmetry along the chain, i.e. finite translations and reflections, as well as rotations by 180 degrees around the center of the chain and reflections in the plane of the carbon rings and perpendicular to the chain with the axis along the chain. The total symmetry group is a direct product of the 1-D symmetries in the axis of the chain and those perpendicular to the chain. If we take the point of view, that the main

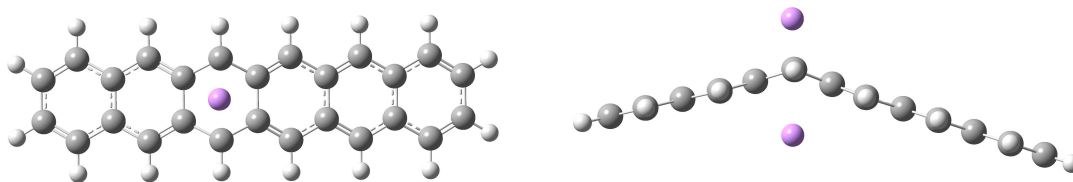


Figure 5: The hexacene molecule with two lithium atoms adsorbed on opposite sides of the third ring.

function of the adsorbed atoms is to donate localized electrons to the chain. then the electron density is no longer translationally invariant. This, according to the arguments of Ruch and Schoenhofer, would lead directly to the symmetry breaking of the other factor in the product. Indeed this is what we observe. The fact, that deflections are larger for centered adsorption pairs might serve as a weak additional hint, as then the ends of the chain are further away and the system is more symmetric to start with.

At this point we have to make two observations:

First, we deal with a direct, rather than a semi-direct product. The argument of [7] is rather subtle, and though it seems to carry through, we plan to formalize it for the special case, and to determine if it falls into the Peierls category.

Second in [5] an alternative rather simple explanation was offered: Bond lengthening is natural as additional negative charge is available. The lengthening is larger for two than for one adsorbed lithium as the transferred charge is larger. For a carbon sheet buckling is expected due to the stiff surroundings, but in the case of polyacenes such bond stretching in the rings could probably be supported without deformation. If the stretching were asymmetric we would expect to see torsion, which we do not see. This latter point is consistent with the configurations found, where the Lithium atoms are very nearly on an axis through the center of the ring, to which they are adsorbed. The alternate explanation of the spontaneous symmetry breaking is therefore not valid in the present case, and thus the argument for a Jahn-Teller or Peierls type behavior is much stronger than the one resulting from the deformations of graphene. This makes us confident, that we indeed see a phenomenon of this type.

5 CONCLUSIONS AND OUTLOOK

After the surprising discovery of spontaneous symmetry breaking in calculations of carbon sheets as aromatic molecules [4, 5] it seemed necessary to get a better handle on the problem by studying a simpler system, quite in the spirit of Marcos Moshinsky. Unfortunately not quite in this spirit is the fact that it is still a numerical study only. The clear and simple numerical result in the case of polyacenes (chains of carbon rings with hydrogen closure) hints strongly to the existence of a simple explanation in terms of a Jahn-Teller or Peierls distortion.

The fact that symmetric adsorption of an alkaline atoms to a carbon ring chain causes a strong

angle to be formed, is a clear and powerful signature of spontaneous symmetry breaking, and as such we expect a simple group-theoretical interpretation. We hinted, that along the argument of Ruch and Schoenhofer this should be possible. Yet, this paper gives a very profound argumentation for the instability of the symmetric systems. In the present, much simpler, case we hope to be able to reduce the argument to a correspondingly simpler form. Thereby we also expect to explore the full scope of the ideas proposed to generalize the Jahn-Teller effect by Ruch and Schoenhofer [7] as well as their reduction to Peierls distortions.

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